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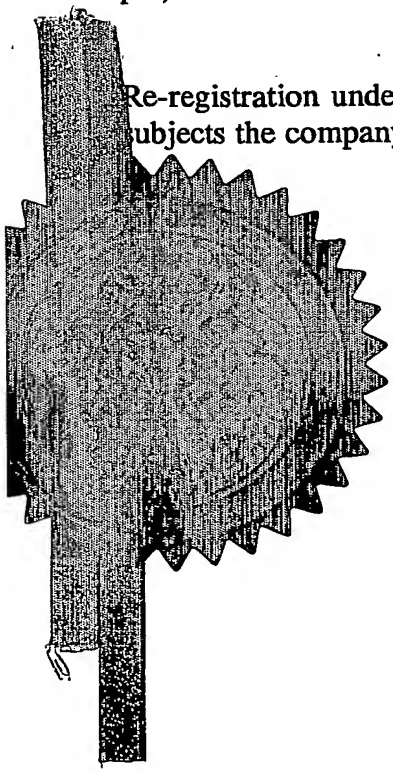
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GB 0222240.4

By virtue of a direction given under Section 30 of the Patents Act 1977, the application is proceeding in the name of

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Incorporated in the United Kingdom,

[ADP No. 08519803001]

25 SEP 2002

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1 Your reference

SYN 51075

2 Patent application number
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0222240.4

3 Full name, address and postcode of the or of
each applicant (underline all surnames)IMPERIAL CHEMICAL INDUSTRIES PLC
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Patents ADP Number (if you know it)

If the applicant is a corporate body, give the
country/state of its incorporation

United Kingdom

4 Title of the invention

COBALT CATALYSTS

5 Name of Your Agent (if you have one)

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Cobalt catalysts

This invention relates to cobalt catalysts comprising cobalt supported on a solid titania support and in particular to a method for manufacturing such catalysts.

5 Catalysts comprising cobalt on a support such as silica or alumina are known in the art for hydrogenation reactions, e.g. for the hydrogenation of chemicals such as aldehydes and nitriles, fats and oils and for the preparation of hydrocarbons from synthesis gas via the Fischer-Tropsch reaction.

WO-A-96/04072 discloses a cobalt on transition alumina catalyst containing between 3 and 40% by weight of cobalt and having a cobalt surface area greater than 30 m²/g cobalt.

10 EP-A-0013275 discloses coprecipitated cobalt-silica hydrogenation catalysts prepared by adding an alkaline precipitating agent to a heated mixture containing cobalt cations, silicate anions and solid porous carrier particles under agitation thereby to precipitate the cobalt and silicate ions onto the solid support particles.

15 EP-A-0029675 discloses coprecipitated nickel hydrogenation catalysts prepared by adding an alkaline precipitating agent to a heated mixture containing cobalt cations, aluminium anions and solid porous particles under to precipitate the nickel and aluminium ions onto the solid support particles.

20 In certain reactions it may be beneficial to use cobalt deposited on a titania support rather than cobalt on alumina because the acid sites present on alumina may promote undesirable reactions, e.g. it may reduce the selectivity to primary amines in the hydrogenation of nitriles. Furthermore titania supported catalyst may be preferred for use in acid reaction media where gamma alumina supports may show a tendency to dissolve to some extent.

25 In comparison with other catalytic metals such as copper and nickel used for hydrogenation reactions, cobalt is a relatively expensive and so, to obtain the optimum activity, it is desirable that as much as possible of the cobalt present is in an active form accessible to the reactants. It is therefore desirable to maximise the surface area of the cobalt in the supported catalysts.

30 Accordingly we now provide a process for manufacturing a catalyst which comprises a cobalt species on a solid titania support, comprising mixing together particles of a solid titania support and an aqueous solution of cobalt ammine carbonate, and heating to an elevated temperature sufficient to effect decomposition of the cobalt ammine carbonate and precipitation of a basic cobalt carbonate onto said support.

35 In one embodiment of the invention we provide a method of making a catalyst comprising a cobalt species on a titania support, comprising the steps of mixing a titania particulate material with an aqueous solution of a soluble cobalt compound, heating the mixture

of particulate material and cobalt compound to effect precipitation of a basic cobalt carbonate species on the titania, filtering the solid residue from the aqueous medium, and drying.

In a further embodiment of the invention we also provide a process for the production of a catalyst comprising saturating titania support particles with an aqueous solution of cobalt ammine carbonate, and removing the excess of the solution, before heating the resulting product to a temperature sufficient to effect decomposition of the cobalt ammine carbonate.

The solid residue comprising the catalyst may be calcined and, optionally, reduced.

The term "cobalt species" is used broadly to include both elemental cobalt and cobalt in combined form, e.g. as compounds such as cobalt oxides and cobalt hydroxycarbonates. The catalyst in its reduced form is useful for catalysing hydrogenation reactions. The catalyst may, however, be provided as a precursor wherein the cobalt is present as one or more compounds, such as oxides or hydroxy carbonates, reducible to elemental cobalt. In this form, the material may be a catalyst precursor and may be treated to reduce the cobalt compounds to metallic cobalt or the material may itself be a catalyst and used as supplied, e.g. for oxidation reactions. The cobalt surface area figures used herein apply to the material after reduction, but the invention is not limited to the provision of reduced catalyst.

By the term total cobalt, we mean the amount of cobalt whether present in elemental or combined form. Generally however at least 70% by weight of the total cobalt in the reduced catalyst will be in the elemental state.

The catalysts of the invention preferably have a cobalt to titanium atomic ratios in the range 0.01 to 50, particularly 0.03 to 25 and especially 0.05 to 10.

The particulate titania may be formed from natural sources or may be a synthetic, e.g. precipitated titania. The particulate titania may be in the form of a powder or a shaped granular material, e.g. as extruded or tabletted titania pieces.

Suitable powdered titanias typically have particles of surface weighted mean diameter $D[3,2]$ in the range 1 to 100 μm , particularly 3 to 100 μm . If desired, the particle size may be increased by slurring the titania in water and spray drying. Preferably the BET surface area of the particles is in the range 10 to 500 m^2/g , particularly 30 to 100 m^2/g .

Granular titanias may have a variety of shapes and particle sizes, depending upon the mould or die used in their manufacture. For example the particles may have a cross-sectional shape which is circular, lobed or other shape and a length from about 1 to 10 mm. The surface area is generally in the range 10 – 500 m^2/g , preferably 100 to 400 m^2/g .

The pore volume of the titania is generally between about 0.1 and 4 ml/g, preferably 0.2 to 2 ml/g and the mean pore diameter is preferably in the range from 2 to about 30 nm.

The cobalt compound is most preferably a cobalt ammine complex which is formed in situ in aqueous solution by dissolving basic cobalt carbonate in a solution of ammonium carbonate in aqueous ammonium hydroxide, to give a product of the desired cobalt content. The cobalt ammine carbonate solution may be made by dissolving basic cobalt carbonate in an aqueous solution of ammonium carbonate containing additional ammonium hydroxide. The relative amounts should be such that the pH of the solution is in the range 7.5 to 12, preferably 9 to 12. The solution preferably contains 0.1 to 2.5 moles of the cobalt complex per litre. As the concentration of cobalt increases, then generally the proportion of carbonate ions relative to hydroxide ions in the basic cobalt carbonate feed should be increased. The cobalt ammine complex compound is then heated, e.g. to a temperature in the range 60 to 110°C, to cause the cobalt ammine complex to decompose with the evolution of ammonia and carbon dioxide and to deposit a basic cobalt carbonate on the surface, and in the pores, of the titania. This step is conveniently carried out when slurring titania powders with the cobalt compound so that the slurry is then maintained at the elevated temperature for a period, hereinafter the ageing period. The solid material is then filtered from the aqueous medium, washed and dried.

The amount of cobalt in the catalyst may be varied by varying the relative amount of cobalt and support present in the reaction mixture and by controlling the concentration of the solution of cobalt compound.

Alternatively the cobalt compound is absorbed into the pore structure of the titania particle by impregnating titania particles with the solution of cobalt compound. The impregnation may be repeated to increase the amount of cobalt compound absorbed by the titania particle, preferably with drying between each impregnation. The particles may then conveniently be separated from the remaining solution and the ageing process may be carried out by heating them e.g. to a temperature above 100°C for the ageing period of at least 60 minutes, preferably at least 100 minutes to decompose the cobalt compound held within the particles to deposit basic cobalt carbonate in the structure of the titania particle. The particle may be subjected to successive impregnations, e.g. by separating them from the impregnation solution and drying before a subsequent impregnation.

The solid material may then be calcined in air, e.g. at a temperature in the range 250 to 450°C, to decompose the basic cobalt carbonate to cobalt oxide. The resultant catalyst precursor may be then reduced, e.g. with hydrogen, at a temperature between 300 to 550°C, more preferably below about 500°C, e.g. 380 to 500°C. Upon reduction, most, if not all, of the cobalt oxide is reduced to metallic cobalt; the result is cobalt metal in a highly dispersed form, i.e. having a high cobalt surface area. Alternatively the basic cobalt carbonate may be directly reduced, i.e. without the need for a calcination step.

Preferably the amounts of titania and cobalt ammine carbonate employed are such that the cobalt to titanium atomic ratio is in the range 0.03 to 5. Irrespective of the cobalt content of

the catalyst, the particle size of the catalyst is essentially the same as the particle size of the titania.

5 The catalysts of the invention preferably contain 3 to 75% by weight of total cobalt, more preferably below 40% by weight total cobalt. The amount of cobalt which is desirable varies according to the type of reaction for which the catalyst is used. Selection of an appropriate amount of cobalt is easily determined or known by the skilled person. Preferred catalysts typically have a cobalt surface area in the range 15 to 100, particularly 20 to 40 m² per gram total cobalt.

10 The cobalt surface area is determined by H₂ chemisorption. The sample (about 0.5 g) is degassed and dried under vacuum at 120°C and then reduced by heating to 425°C at a rate of 3°C per minute whilst hydrogen gas is passed through the sample at a flow rate of 250 ml/min for 18 hours. The sample is then heated under vacuum to 450°C over 10 minutes and maintained under those conditions for 2 hours. Following this pre-treatment, the chemisorption analysis is carried out at 150°C using pure H₂ gas. The full isotherm is measured up to 800 mm Hg pressure of H₂ and the straight line portion of the chemisorption isotherm between 300 and 800 mm Hg is extrapolated to zero pressure to calculate the volume of the gas (V) which is chemisorbed by the sample. The metal surface area is then calculated from the following equation:

$$\text{Co surface area} = (6.023 \times 10^{23} \times V \times \text{SF} \times A) / 22414$$

20 where V = uptake of H₂ in ml/g

SF = Stoichiometry factor (assumed 2 for H₂ chemisorption on Co)

A = area occupied by one atom of cobalt (assumed 0.0662 nm²)

25 This method of calculating cobalt surface area is described in the Operators Manual for the Micromeritics ASAP 2000 Chemi System V 1.00, Appendix C, (Part no 200-42808-01, 18th January 1991)

30 For hydrogenation reactions, the active form of the cobalt is elemental cobalt although in the active catalyst only some, rather than all, of the cobalt is normally reduced to the elemental form. Hence a useful measure is the exposed surface area of elemental cobalt per g of total cobalt present. Except where expressly indicated, as used herein, total cobalt contents are expressed as parts by weight of cobalt (calculated as cobalt metal, whether the cobalt is actually present as the metal or is in a combined form, e.g. as cobalt oxides) per 100 parts by weight of the catalyst or precursor thereto.

Useful catalyst products are formed by the dried precipitated product, a calcined (oxidic) product or a reduced product, depending on the use for which the catalyst is made.

When a catalyst composition requires a step such as calcination and/or reduction to produce the active form of catalyst for the desired reaction, it may be referred to as a catalyst precursor.

5 In a non-reduced form the catalysts may be useful in oxidation reactions e.g. to oxidise organic compounds, for example as in the treatment of effluent containing organic material.

The catalysts, in reduced form, may be used for hydrogenation reactions such as the hydrogenation of aromatic or olefinic compounds, e.g. waxes, nitro, nitrile or carbonyl compounds, e.g. the conversion of nitrobenzene to aniline or the conversion of nitriles to amines or the hydrogenation of aldehydes to the corresponding alcohols. They may also be used for the hydrogenation of paraffin waxes to remove traces of unsaturation therein. They may also be useful in a wide range of other reactions, for example the Fischer-Tropsch process, i.e. where hydrogen and carbon monoxide are reacted in the presence of the catalyst to form higher hydrocarbons. This may be part of an overall process for the conversion of natural gas to petroleum compounds wherein the hydrogen / carbon monoxide gas mixture is a synthesis gas formed by steam reforming natural gas. The catalysts are particularly suitable for use in hydrogenation reactions, e.g. the hydrogenation of fatty nitriles and aldehydes.

The catalyst may be provided in the form of a concentrate of the catalyst particles dispersed in a suitable carrier medium, e.g. hardened soybean oil. Preferably the amount of catalyst in said concentrate is such that the concentrate has a total cobalt content of 5 to 30%, preferably 10 to 25% by weight.

When the catalyst is to be used in a reduced form, it may be supplied in non-reduced form, i.e. as a catalyst precursor, to be reduced in-situ before use or alternatively the catalyst may be reduced and then passivated in order to protect the reduced metal during subsequent storage and transport. Methods of protecting the catalyst are well known.

25 The invention is illustrated by the following examples in which the stock solution employed was made up using 1707 g ammonia solution (SG 0.89, 30% ammonia), 198 g ammonium carbonate, 218 g basic cobalt carbonate (46.5% wt% Co, bulk density 0.640 g/ml) and 1877 g demineralised water. The total volume of the stock solution was 4 litres.

30 The carrier employed was P25 titania supplied by Degussa, having a surface area of $50.6 \text{ m}^2/\text{g}$ and a pore volume (as determined by nitrogen porosimetry from the P/Po values of the desorption isotherm) of about 0.14 ml/g and having a mean diameter $D[3,2]$ of $1.7 \text{ }\mu\text{m}$. The average pore diameter was about 11.5 nm.

Example 1.

35 A portion of the stock solution was diluted with 7 parts by volume of a 9 wt% ammonia solution per part by volume of the stock solution in order to reduce the viscosity of the slurry

produced by mixing the solution with the carrier particles.. The pH of the diluted stock solution was 11.1.

5 The titania carrier particles and an amount of the diluted stock solution corresponding to a nominal 5% by weight of cobalt, based on the weight of the titania particles, were charged to a stirred vessel equipped with a condenser. The mixture was heated to boiling while stirring and gentle boiling at about 96°C was maintained for a period of time. After about 90 min total heating time the solution became clear. After a total heating time of 130 min part of the mixture was filtered and the solid recovered, washed and then dried in air at 110°C overnight so give sample A.

10 The gentle boiling was continued for the remaining portion of the mixture for a further 20 min (to give a total heating time of 150 min) and then the mixture was filtered and the solid recovered, washed and then dried in air at 110°C overnight so give sample B.

15 The resultant catalyst precursors A and B were then reduced by passing hydrogen through a bed of the catalyst while heating to 430°C. The cobalt surface area was determined by H₂ chemisorption as described hereinbefore.

Example 2

Example 1 was repeated, but using undiluted stock solution and total heating times of 130 and 150 min. The amount of stock solution employed was such as to give a nominal 10% by weight of cobalt, based on the weight of the titania particles.

20 Example 3

Example 1 was repeated but using 1 part by volume of the 9 wt% ammonia solution per part by volume of the stock solution, and an amount of the diluted stock solution such as to give a nominal 15% by weight of cobalt, based on the weight of the titania particles. The total heating times were 120, 140 and 160 min.

25 Example 4

Example 2 was repeated, using undiluted stock solution in such an amount that the nominal cobalt content was 20% by weight based on the weight of the titania particles. The total heating times were 70, 95, 120 and 135 min.

Example 5

30 Example 1 was repeated but using 1 part by volume of the 9 wt% ammonia solution per part by volume of the stock solution, and an amount of the diluted stock solution such as to give a nominal 25% by weight of cobalt, based on the weight of the titania particles. The total heating times were 60, 80 and 100 min.

The cobalt content of the reduced catalyst was calculated from the measured cobalt content of the unreduced material and the weight difference between the unreduced material and the reduced catalyst. The chemisorption results are shown below

Example	Heating time (min)	Cobalt content (% wt)		Cobalt surface area	
		Precursor before reduction	Reduced catalyst	m ² per g of reduced catalyst	m ² per g of cobalt
1A	130	5.5	5.8	1.0	17
1B	150	5.4	5.6	1.4	25
2A	130	10.1	11.0	2.5	23
2B	150	10.0	11.0	1.9	17
3A	120	15.9	17.8	4.1	23
3B	140	16.0	17.8	3.9	22
3C	160	16.0	17.8	3.8	21
4A	70	16.1	18.1	4.6	25
4B	95	20.8	24.2	4.0	17
4C	120	21.1	24.6	5.4	22
4D	135	21.1	24.6	5.1	21
5A	60	26.4	31.4	6.4	20
5B	80	27.4	32.7	4.1	13
5C	100	27.7	32.5	5.7	18

- 5 A sample of the precursor, i.e. before reduction, of Example 4D was subjected to temperature programmed reduction which gave peaks at 195°C, 275°C and 435°C. The 275°C peak probably is reduction of Co₃O₄ to CoO while the 435°C peak corresponds to reduction of CoO to the cobalt metal. There is no evidence for any species reducing at high temperatures

suggesting that all cobalt may be reducible and that there is little risk of unreducible cobalt titanate formation.

Claims.

1. A process for manufacturing a catalyst which comprises a cobalt species on a solid titania support, comprising mixing together particles of a solid titania support and an aqueous solution of cobalt ammine carbonate, and heating to an elevated temperature sufficient to effect decomposition of the cobalt ammine carbonate and precipitation of a basic cobalt carbonate onto said support.
2. A process as claimed in claim 1, comprising saturating titania support particles with an aqueous solution of cobalt ammine carbonate, and removing the excess of the solution, before heating the resulting product to a temperature sufficient to effect decomposition of the cobalt ammine carbonate.
3. A process as claimed in claim 1, wherein the mixture of solid support and said cobalt solution is heated to a temperature sufficient to effect decomposition of the cobalt ammine carbonate in situ before separating the solid catalyst from the mixture and drying.
4. A process as claimed in any of claims 1 to 3, wherein the solid support and cobalt solution are maintained at an elevated temperature for a period of at least 60 minutes.
5. A process as claimed in any of claims 1 to 4, wherein said temperature is in the range 60 to 110°C.
6. A process as claimed in any of claims 1 to 5, further comprising the step of calcining the resulting product at a temperature between 200 and 600°C.
7. A process as claimed in any of claims 1 to 6 further comprising the step of reducing the resulting product with hydrogen at a temperature between 300 to 550°C.
8. A process for the production of a catalyst comprising heating a slurry of particles of titania suspended in an aqueous solution of a cobalt ammine carbonate for a total period of at least 60 minutes at a pH above 7.5 at an elevated temperature sufficient to effect decomposition of the cobalt ammine carbonate and precipitation of a basic cobalt carbonate, and thereafter filtering the precipitated basic cobalt carbonate residue from the aqueous medium.

9. A catalyst or catalyst precursor made by the process claimed in any of claims 1 to 8.
10. A process for the hydrogenation of an organic compound comprising an olefinic, carbonyl, nitrile, nitro or aromatic group, comprising reacting said compound with hydrogen in the presence of a catalyst as claimed in claim 9.
11. A process for the formation of a hydrocarbon by the reaction of carbon monoxide with hydrogen in the presence of a catalyst as claimed in claim 9.
12. A process as claimed in claim 10 or claim 11 further comprising the step of forming an active catalyst in situ by reducing a catalyst precursor as claimed in claim 9 with hydrogen before conducting said hydrogenation reaction.
13. A process for the oxidation of an organic compound by reaction with an oxygen-containing compound in the presence of a catalyst as claimed in claim 9.

Abstract

Catalysts comprising cobalt on a titania support are produced by mixing together particles of a solid titania support and an aqueous solution of cobalt ammine carbonate, and heating to an elevated temperature sufficient to effect decomposition of the cobalt ammine carbonate and precipitation of a basic cobalt carbonate onto said support.

